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Molecular dynamics study of the vulcanization transition

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We report on extensive computer simulations of randomly cross-linked polymer networks in the vicinity of the liquid-solid transition. We have determined the order parameter and the distribution of localization lengths as a function of cross-link density n near the critical point for up to $M=500$ chains of length $N=10$ and $M=100$ chains of length $n=20$. We find that the order parameter varies as $q(n)\sim n-n_c$, in agreement with the classical and modern theories of rubber elasticity and that the distribution of localization lengths assumes a universal form, in agreement with recent predictions. [S1063-651X(98)05609-8]

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I. INTRODUCTION

When polymers in a dense melt are irreversibly cross-linked a phase transition from a liquid state to an amorphous solid state occurs if the density of cross-links is sufficiently high. This is the vulcanization transition, which has been studied both experimentally and theoretically for many years [1]. The classical theories of rubber elasticity [2] consist essentially of Gaussian polymer theory combined with the mean field theory (Bethe lattice) of percolation. It is only since the 1970s, beginning with work of de Gennes [3] that ideas originating in the modern theory of critical phenomena have been applied to the vulcanization transition. More recently, Goldbart and collaborators [4] building on work of Edwards and co-workers [5] have constructed a replica theory of the vulcanization transition that treats the percolative aspects and the quenched disorder introduced by the random cross-links in a unified way. This new theory has produced a number of specific predictions. Of interest for this paper are the following: (i) the critical density of cross-links $n=N_{\mathrm{cl}}/M\approx 1.0$ where N_{cl} is the number of cross-links and M is the number of chains, (ii) the order parameter q (to be defined below) varies near the critical cross-link density as $q\sim n-n_c$, and (iii) there exists a universal distribution of localization lengths $P(\xi)$ in the amorphous phase, at least sufficiently close to n_c. Predictions (i) and (ii) are consistent with the classical theories of vulcanization albeit derived by quite different reasoning but (iii) is unique to the newer theory.

Motivated by these developments, we began some time ago to investigate the vulcanization transition by molecular dynamics simulations. In a first paper [6], we studied relatively small numbers of chains of various lengths and calculated the order parameter and distribution of localization lengths. Our results for the order parameter were $q\sim(n-n_c)^{\beta_q}$ with an exponent $\beta_q\approx 0.5$, i.e., inconsistent with one of the aforementioned predictions. On the other hand, the distribution of localization lengths, when plotted in terms of an appropriate scaled variable proved to be essentially independent of the relevant parameters such as chain length and number of cross-links. In these simulations, the determination of the critical cross-link density was rather imprecise and the exponent β_q also quite uncertain. The largest system consisted of 100 chains of length $N=10$ and the range of cross-link densities over which the percolation probability drops from 1 to a small number is extremely wide. Presumably, the same is true of the range of densities over which vulcanization occurs (if these are different). The same difficulties plagued a later calculation of the critical behavior of the shear modulus [7]. Since this particular finite-size effect depends on the number of chains and not on the length of the chains, we have chosen, in the present work, to work with short chains and to increase, as much as our resources permit, the number M of chains.

We report, in this paper on the calculation of the order parameter and the distribution of localization lengths for chains of length $N=10$ and numbers of chains $M=200$, 300, and 500. We also include, for comparison, results for a system of 100 chains of length $N=20$. These larger systems all have a critical cross-link density very close to $n_c=1$ and an exponent $\beta_q\approx 1$. Moreover, the distribution of localization lengths is now in remarkably good agreement with the predictions of [4]. One remaining puzzle is that the critical cross-link density, as determined from the point at which the order parameter vanishes, is measurably above the cross-link density at which geometric percolation occurs. However, there are some indications that this may be a finite size effect.

The structure of this article is as follows. In Sec. II we briefly describe the model, computational techniques, and some aspects of the data analysis. Section III contains the results and we conclude in Sec. IV with a brief discussion and an outlook for future work.

II. MODEL AND COMPUTATIONAL TECHNIQUES

A. Hamiltonian and computational details

For completeness, we briefly describe our model of polymers, which is identical to that used by Kremer, Grest, and collaborators [8] in their simulations. All particles in the system interact through a purely repulsive 6-12 potential:

$$U_{LJ}(r_{ij})=\begin{cases}4\epsilon\left[\left(\dfrac{\sigma}{r_{ij}}\right)^{12}-\left(\dfrac{\sigma}{r_{ij}}\right)^{6}+\dfrac{1}{4}\right], & r_{ij}<2^{1/6}\sigma\\ 0, & r_{ij}\geqslant 2^{1/6}\sigma.\end{cases} \tag{1}$$

Tethering of the N particles on each chain is enforced by the attractive potential [9]

$$U_{nn}(r_{ij})=\begin{cases}-\dfrac{1}{2}kR_0^2\ln\left[1-\left(\dfrac{r_{ij}}{R_0}\right)^{2}\right], & r_{ij}<R_0\\ \infty, & r_{ij}\geqslant R_0,\end{cases} \tag{2}$$

where $R_0=1.5\sigma$ and $k=30\epsilon/\sigma^2$. With these parameters, chains are unable to cut through each other.

In contrast to our previous constant energy molecular dynamics calculations, we have here used a Brownian dynamics scheme at a temperature $k_bT/\epsilon=1$ with a time step $\delta t=0.012\sqrt{m\sigma^2/\epsilon}$ and a standard velocity Verlet algorithm for the integration of the equations of motion [10]. The systems were equilibrated as polymer melts at a density $\rho\sigma^3=0.85$, where $\rho=NM/V$, with V the volume of the computational box. Periodic boundary conditions were used.

After equilibration, permanent cross-links were imposed on the system by randomly selecting pairs of monomers within a distance of 1.25σ of each other and tethering them together by means of the potential (2). Any pair of particles, except nearest neighbors on the same chain, were considered eligible. Thus there were invariably a certain number of self-linkages, i.e., cross-links between distant monomers on the same chain [11]. The new equations of motion were then integrated, typically for $(8-9)\times10^6$ and in some cases for 3.6×10^7 time steps. The desired physical quantities were obtained from averages over 10–25 independent realizations of the same fixed number of cross-links.

B. Measured quantities

For each of the monomers j in the system, we calculated the time average of the quantity $q_{\mathbf{k}}(j)=\exp\{i\mathbf{k}\cdot\mathbf{r}_j\}$, i.e.,

$$q_{\mathbf{k}}(j,t)=\frac{1}{t}\sum_{t'=1}^{t}e^{i\mathbf{k}\cdot\mathbf{r}_j(t')}. \tag{3}$$

Here $\mathbf{k}=(2\pi/L)(n_x,n_y,n_z)$ where L is the length of a side of the cubic computational box and n_α integers. We used only the three smallest available $\mathbf{k}$ vectors [(1,0,0), (0,1,0), (0,0,1)] and, in the end, averaged the three sets of results. The order parameter of the system is then given by

$$q_{\mathbf{k}}(n)=\frac{1}{NM}\sum_j\,\left|\lim_{t\to\infty}q_{\mathbf{k}}(j,t)\right|^2, \tag{4}$$

where the sum is over all monomers in the system. For reasons discussed in [6], we constructed a series of partial time averages $q(n,t)$:

$$q(n,t)=\frac{1}{3NM}\sum_{\mathbf{k}}\sum_j\,|q_{\mathbf{k}}(j,t)|^2\ . \tag{5}$$

This function has initial value $q(n,1)=1$ and decreases towards its asymptotic value as t increases. For heavily cross-linked systems it is possible to carry out a long enough MD run that this asymptotic value is clearly attained. On the other hand, in the critical region the longest relaxation time is considerably longer than our computational limit and it is necessary to extrapolate $q(n,t)$ to $t=\infty$. This potentially problematic extrapolation is discussed in the next subsection.

We have also determined the distribution of localization lengths. In the amorphous phase, each monomer j that is part of the rigid structure is typically free to fluctuate over some distance ξ_j. If the probability of finding particle j at a given point $\mathbf{r}_j$ is described by the isotropic Gaussian probability density

$$\widetilde{P}(\mathbf{r}_j)=\frac{1}{\pi^{3/2}\xi_j^{3/2}}\exp\left\{-\frac{|\mathbf{r}_j-\overline{\mathbf{r}}_j|^2}{\xi_j^2}\right\}\ , \tag{6}$$

then the partial order parameter for particle j, $|q_{\mathbf{k}}(j,t)|^2$, is given by $\exp(-k^2\xi_j^2/2)$ and from this relation we may obtain the localization length $\xi_j(t)$ and a histogram of the function $P(\xi(t))$. The time dependence in ξ and therefore $P(\xi)$ comes from the fact that the MD simulation is, in general, terminated before the order parameters have attained their asymptotic values. However, it transpires that the distribution P when plotted as function of the scaled variable $\xi/\overline{\xi}(t)$, where $\overline{\xi}(t)$ is the mean localization length calculated from the order parameters averaged to time t is independent of t to an excellent approximation [6] and we are confident that the reported distribution of localization lengths represents the infinite time limit.

C. Data analysis

The extrapolation of the running average $q(n,t)$ to the infinite time limit is a potential source of error and we therefore discuss it here in some detail. In our previous simulations [6] we had noticed that if we plotted $q(n,t)$ against $t^{-1/2}$, the data seemed to approach a straight line at long times. However, there is no convincing theoretical argument for this behavior and the extrapolation must therefore be examined critically. For samples that are clearly in the rigid regime, one can attempt to fit the data to a function of the form $q(n,t)=q_0+at^{-\phi}$ and we have done this for a number of data sets. Although the estimates of ϕ are not very precise, they are generally in the vicinity of $\phi=0.5$. Another approach is to assume that ϕ is independent of the cross-link density n and attempt to determine it from log-log plots of $q(n,t)$ for samples that, by any reasonable method of extrapolation, clearly are fluid and for which $q(n,t)$ should display a power-law decay. Figure 1 shows such a plot for four different samples of 200 polymers of length 10 in the critical region. The data points do seem to fall asymptotically on a straight line with slope $\phi\approx1/2$.

In the amorphous phase, we have generally fitted the data to $q(n,t)=q_0+at^{-1/2}+bt^{-1}$ in order to take into account the curvature of the data at early times. To test the reliability of this procedure, we have run the simulations for a number of samples for much longer times than the standard 8×10^6 time steps (for 200 polymers) and compared the extrapolated values from shorter runs to those obtained from longer runs. Such a comparison is shown in Fig. 2 for 200 chains of

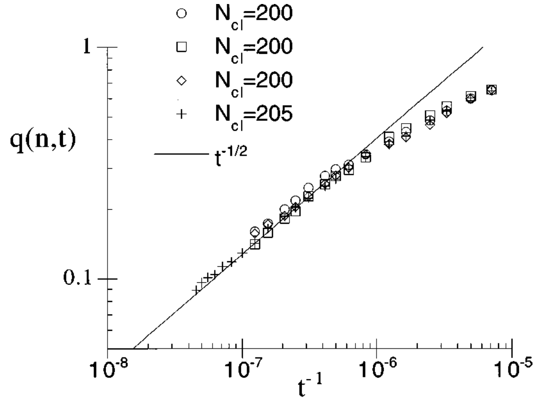

FIG. 1. Plot of the running average $q(n,t)$ for a set of samples of 200 chains of length 10 in the critical region. All reasonable methods of extrapolation yield $q(n,\infty)=0$ for these samples. For long times the data are consistent with the functional form $q(n,t) \sim t^{-1/2}$.

length 10 with two samples, each with $N_{cl}=250$ cross-links. There are two noteworthy features to this figure. First, we see that the fluctuation of the order parameter from sample to sample is extraordinarily large: The extrapolated values for these two cases differ by almost a factor of 2. On the other hand, the estimates of q_0 obtained from runs of 2.4×10^7 time steps differ only by a few percent from those obtained from runs a factor of 3 shorter. It is also reassuring that there is no systematic trend: In one case, the estimate of q_0 is raised with the addition of more data, in the other case it is lowered. We are therefore of the opinion that the uncertainties in our estimate of the order parameter are primarily due to the fluctuations generated by the random nature of the cross-linkings and to a much lesser extent due to the extrapolation procedure.

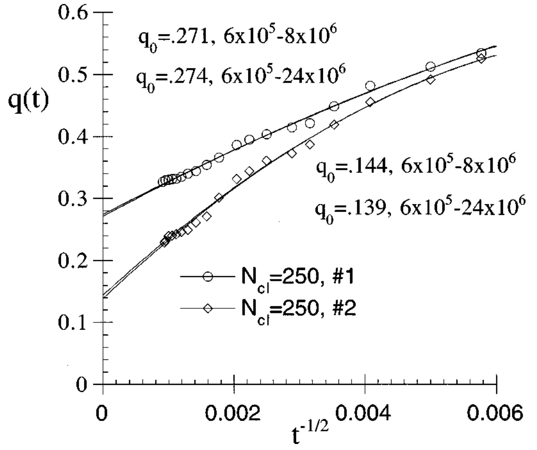

FIG. 2. Test of the extrapolation procedure $q(t)=q_0+at^{-1/2}+bt^{-1}$ for two systems of 200 polymers of length 10 with $N_{cl}=250$ cross-links. The MD simulation was carried out for 2.4×10^7 time steps. The first set of extrapolations uses the data for $q(n,t)$ for $6\times10^5 \le t \le 8\times10^6$; the second pair uses the remaining data. We note that the differences between the two estimates of q_0 for each system is quite small, especially when compared to the difference between the two asymptotic values of q_0 and that there is no systematic trend to either lower or higher estimates when more data is added.

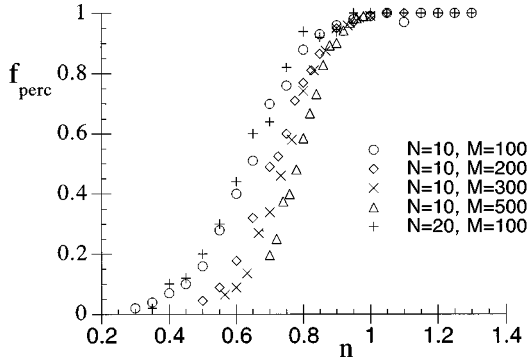

FIG. 3. The probability that geometric percolation occurs as a function of cross-link density for chains of length $N=10$. The critical concentration is $n_{perc}\approx0.95$.

III. RESULTS

As mentioned in the Introduction, we are interested in investigating the behavior of cross-linked polymers in the critical region and therefore have concentrated our efforts toward increasing the number M of chains rather than the chain length N. The reason for this is partly shown in Fig. 3 where the fraction of samples that percolate in all three directions is plotted as a function of cross-link density for chains of length 10 for $M=100$ to $M=500$. For comparison we have also shown the percolation probability for 100 chains of length 20, which falls essentially on top of the data for 100 chains of length 10. It is clear that the transition region, which one could define, for example, to be the range of cross-link densities over which f_{perc} increases from 0.25 to 0.75 narrows substantially as the number of chains is increased from 100 to 500. The critical concentration for percolation can be estimated from the intersection of the functions $f_{perc}(n)$ for different values of M. This occurs at $n_{perc}\approx0.95$.

We have carried out extensive MD simulations, as described above, for the systems of size $M=200$ and 300 and have simulated a few cross-link densities in the critical region for $M=500$. For the system of 200 chains, we have typically used 25 different realizations of the same cross-link density to obtain the order parameter and have generally used integration times of 8×10^6 MD steps. For the system of 300 chains, we have averaged over 16 different realizations of the cross-linkings and integrated the equations of motion for a minimum of 9×10^6 time steps. In the case of 500 chains, the integration time was 1.5×10^7 time steps. In studying such short chains, we are focusing on a regime in which the effects of entanglements should be insignificant [12]. Moreover, it is possible that the transition from the liquid to the amorphous phase may be in the percolative universality class rather than in the vulcanization universality class, which is associated with the limit $N\to\infty$ [3,13].

The results for the order parameter are shown in Fig. 4. Although the data are quite noisy, due to the small number of realizations for each cross-link density, taken together they provide quite strong evidence for a linear dependence of the order parameter on n. For both 200 chains and 300 chains, the median value of the extrapolated order parameter is zero at $n_c=1.0$ [14]. Indeed, the fit of the data for $M=200$ to the functional form $q=a(n-n_c)^{\beta_q}$ yields $n_c=1.01$, $\beta_q=0.99$.

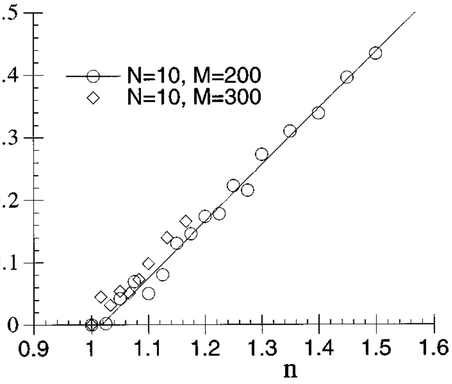

FIG. 4. The order parameter $q(n)$ as a function of cross-link density $n=N_{\mathrm{cl}}/M$ for $N=10$ and $M=200$, 300. The solid line is a fit of the data for $M=200$ to $q(n)=a(n-n_c)^{\beta}$, which yields $n_c=1.01$, $\beta=0.99$.

The data for $M=300$ are too sparse to permit a three-parameter fit, but since they are interleaved between the points for $M=200$, it is clear that $n_c=1$, $\beta_q\approx 1$ adequately describes both systems. For comparison, we show in Fig. 5 the order parameter for $N=10$, $M=200$ together with the order parameter for the system of 100 chains of length 20. These data are also consistent with a linear dependence of q on $n-n_c$ and demonstrate how the longer floppy segments between cross links reduce the magnitude of the order parameter.

The critical concentration of cross links $n_c\approx 1.0$ obtained from $q(n)$ is somewhat higher than the percolation concentration $n_{\mathrm{perc}}\approx 0.95$. What makes this result puzzling is that n_{perc} obtained from the intersection of the percolation probabilities for different numbers of chains is, in fact, a generally reliable and stable method of estimating the percolation concentration in the thermodynamic limit $M\to\infty$. It is clear from Fig. 3 that for $n=1.0$, all but a very small subset of samples percolate in all three directions. Nevertheless, for both $M=200$ and $M=300$ less than half display a finite value of q. To further investigate whether or not this is a finite size effect, we have generated a number of samples for $N=10$, $M=500$ in the vicinity of $n=1$. Preliminary results are that the order parameter is finite at $n=1.0$ and is equal to zero at $n=0.96$. It can therefore not be ruled out that $n_c=n_{\mathrm{perc}}$ in the thermodynamic limit, consistent with the general view that the onset of rigidity and geometric percolation coincide, except possibly at $T=0$ [15].

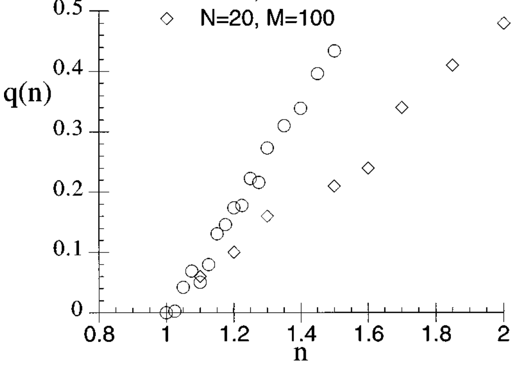

FIG. 5. Order parameter for 100 polymers of length 20 together with the corresponding data for 200 polymers of length 10. Although the longer polymers are floppier, the critical cross-link density and linear variation with n are consistent with that of the $N=10$ system.

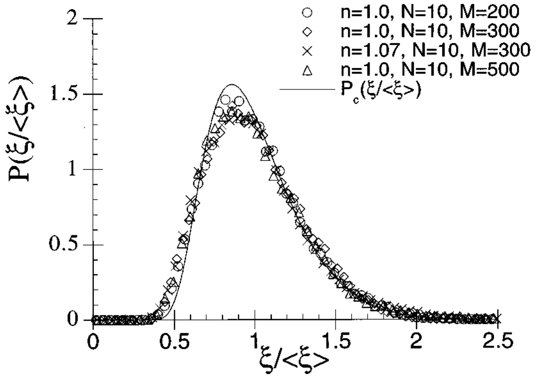

FIG. 6. The probability distribution of localization lengths of monomers connected to the largest cluster in a given sample, together with the predicted universal function of [4] (solid line).

As discussed in Sec. II, we have also calculated the distribution of localization lengths. In contrast to our previous work [6], we have used only those monomers that are connected to the largest (percolating) cluster in the system and ignored the remaining particles. This means that particles that are localized solely due to entanglements are not taken into account. On the other hand, this procedure removes a secondary peak at large ξ, which is due to freely drifting chains. As mentioned above, the distribution of localization lengths, when plotted as a function of $\xi/\langle\xi\rangle$, is quite insensitive to the cutoff time in the MD run and should be regarded as characteristic of the equilibrium state. In Fig. 6, we show this scaled distribution function for polymers of length $N=10$ together with the universal function $P(\xi)$ derived by Goldbart *et al.* [4], scaled in the same way. In contrast to our previous results for smaller systems and with the free polymers included, the theoretical curve and simulation results are in remarkable agreement. It is particularly noteworthy that the simulations support the notion of universality: curves for different cross-link densities do fall essentially on top of each other. Similarly, Fig. 7, in which $P(\xi)$ is plotted for chains of length 10 and 20, shows that the scaled distribution is insensitive to chain length.

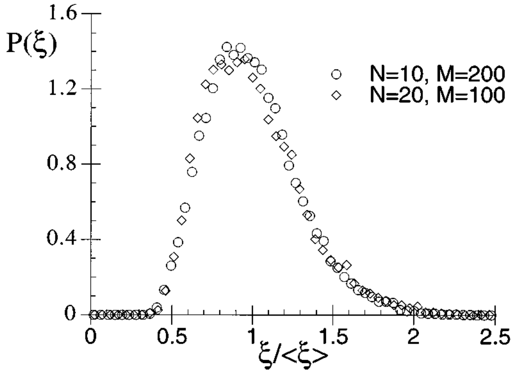

FIG. 7. Plot of the distribution of localization lengths for 100 polymers of length 20 together with that for 200 polymers of length 10, both for $n=1.0$ cross-links per polymer. This plot again shows that $P(\xi)$ is insensitive to microscopic details.

IV. DISCUSSION

Our results to date seem to provide substantial support for the theory of vulcanization proposed by Goldbart and collaborators [4]. While the agreement of the critical cross-link density $n_c \approx 1$ and the exponent $\beta_q \approx 1$ with their predictions is quite pleasing, it must be acknowledged that simulations of the size reported here can by no means be regarded as conclusive as far as determination of critical parameters and exponents is concerned. Even for the system of 500 chains, we are in the best of circumstances only able to vary the cross-link density in steps $\delta n \geqslant 0.002$ and this is a measure of how close we can expect to come to the critical point. With our resources, it would be prohibitively time consuming to attempt a determination of n_c to this accuracy, given the large fluctuations between different cross-linkings that are exhibited in Fig. 2 and in the noise in Fig. 4. On the other hand, we believe that our results for the distribution of localization lengths are robust and these are in remarkable agreement with the predictions.

A number of important issues remains to be addressed as far as this simulation work is concerned. First, it will be important to carry out reliable calculations of the elastic constants for cross-linked polymers. Our previous work [7] has shown that the calculation of elastic constants for the present model is even more difficult than the calculation of the order parameter in that the fluctuations are yet larger. In this context, it may be worthwhile to consider a less faithful model of the physical cross-linking process [11] in hopes of achieving better convergence while still remaining within the same universality class.

Another important issue is the question of replica symmetry breaking or ergodicity breaking. The randomly imposed permanent cross-links constitute a set of quenched random variables analogous to fluctuating exchange constants in the case of spin glasses. Although the existing analytic theories are replica symmetric and although our previous small-scale simulations [6] did not display replica symmetry breaking, it will nevertheless be interesting to investigate this aspect by further simulations. Calculations of the overlap distribution are presently in progress [16].

Finally, we return to the issue of chain length and the nature of the vulcanization transition. de Gennes [3] has argued, on the basis of a Ginzburg criterion, that in the limit $N \rightarrow \infty$, percolation is a classical or mean field transition. Moreover, his argument predicts that the range of cross-link densities δn in which fluctuations dominate scales as $\delta n/n_c = aN^{-1/3}$ in three dimensions, where the unknown prefactor a is presumably nonuniversal. This would seem to indicate that in our case ($N=10$) fluctuations could be important in a significant range of cross-link densities unless a is very small, and that we should expect to observe the three-dimensional percolation exponents, e.g., $\beta \approx 0.43$. This issue has been previously addressed by Grest and Kremer [17] who studied percolation of cross-linked polymers using precisely the same model as we do. Their simulations, for chains of length $25 \leqslant N \leqslant 200$, showed no evidence of nonclassical exponents even for the shortest chain length. Thus there is good evidence that for this model the prefactor a, and thus the critical region, is indeed quite small.

We also point out that the order parameter $q(n)$ is technically not the same quantity as the order parameter $P_\infty(n)$ [18], the probability that a given chain is part of the percolating cluster, of geometric percolation. The difference is due to the dependence of the average localization length $\overline{\xi}$ on the cross-link density. As $n \rightarrow n_c$, $\overline{\xi} \rightarrow \infty$, at least in the thermodynamic limit $M=\infty$ and this effect serves to make $q(n)$ decrease more rapidly than P_∞ as $n \rightarrow n_c$. Thus, we believe it is an open question whether or not the two order parameter exponents β should be the same even if chains of length $N=10$ are in the percolative universality class.

The crossover between the percolative and mean field universality classes has also been observed in experiments on gelation [19,20] where measured exponents typically fall between the predictions of the two models. However, systems with a very small degree of polymerization ($N \approx 2$) [13] seem to be quite clearly in the percolation universality class.

ACKNOWLEDGMENTS

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[11] There is no *a priori* reason for excluding self-linkages since they would certainly occur in real vulcanization processes.

However, there are indications [B. Joós (private communication)] that excluding self-linkages reduces fluctuations in measured quantities and narrows the critical region. Therefore, this may be a useful modification of the model.

[12] The entanglement length for polymer melts at density $\rho\sigma^3 = 0.85$ has been estimated by [8] to be $N_e \approx 35$.

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[14] The order parameter q as defined in 4 is obviously positive semi-definite. However, the partial time averages $q(n,t)$ are noisy functions due to the Brownian dynamics and the random nature of the cross-linking process. Therefore, it is possible for the extrapolation procedure to produce an estimate $q_0 < 0$.

[15] It is well known that at $T=0$, diluted central force networks have a separate rigidity percolation point at a substantially higher concentration of sites or bonds than is necessary for geometric percolation. [See, for example, S. Feng and P. N. Sen, Phys. Rev. Lett. **52**, 216 (1984) or D. J. Jacobs and M. F. Thorpe, Phys. Rev. E **53**, 3682 (1996) for more recent developments.] However, at zero temperature rigidity is a purely energetic effect whereas at finite T there is generically an entropic contribution to the elastic constants. In diluted central-force networks at finite T, geometric and rigidity percolation coincide [M. Plischke and B. Joós, Phys. Rev. Lett. **80**, 4907 (1998)].

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